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CO₂ Hydrogenation on Cu/Al₂O₃: Role of Metal/Support Interface in Driving Activity and Selectivity of a Bifunctional Catalyst

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1 Introduction

The hydrogenation of CO₂ into CH₃OH has been identified as a very promising route to mitigate the increasing anthropogenic CO₂ content in the atmosphere by incorporating CO₂ into a carbon-cycle, in the so-called methanol economy, provided that i) hydrogen is derived from green technology, e.g. water electrolysis using excess intermittent energy, and ii) efficient CO₂ capture technologies are available.^[1-3] In that regard, copper-based catalysts are good candidates in terms of activity and selectivity for transforming CO₂ to CH₃OH.^[1] However, the efficiency of the CO₂-to-CH₃OH synthesis can be significantly decreased by the competitive reverse-water-gas-shift (RWGS) reaction that transforms CO₂ into CO in addition to the thermodynamic limits of the reaction (~20% conversion at 230 °C and 30 bar). Among Cu-based catalysts, Cu/ZnO/Al₂O₃ and Cu/ZrO₂ have been shown to be effective in the selective hydrogenation of CO₂ to CH₃OH.^[1, 4-11]

For Cu/ZrO₂, the selective CO₂ hydrogenation to CH₃OH is ascribed to Lewis acidic Zr(IV) surface sites, located at the periphery of Cu nanoparticles that facilitate the formation of formate and methoxy reaction intermediates.^[12-13] For comparison, Cu/SiO₂ that does not contain Lewis acidic sites shows significantly lower activity and selectivity favoring CO formation. In fact, introducing surface Zr(IV) or Ti(IV) sites on SiO₂ at the interface with Cu nanoparticles via Surface Organometallic Chemistry (SOMC) increases the CH₃OH activity and selectivity, further supporting the importance of Lewis acid sites in this reaction.^[13-14] Regarding CO, it has mainly been proposed to be formed on copper-based catalysts via two different mechanisms: The so-called redox and formate pathways. The former consists of the direct conversion of CO₂ to CO (that may involve M-COOH intermediates) and the subsequent reduction of Cu₂O surface species to Cu(0) metal forming H₂O, while the latter involves the

decomposition of formate into CO.^[9, 15-27] Additionally, the formation of CO but also CH₃OH is often proposed to be related to the presence of oxygen defect sites originating from the oxide support.^[28-36]

For Cu/ZnO/Al₂O₃, the origin of the promotional effect towards selective CH₃OH formation is still a matter of debate. For instance, CuZn alloy or the Cu/ZnO interface has been proposed to generate the active site responsible for the high CH₃OH selectivity.^[37-44] In contrast, Al₂O₃, a minor component of the catalyst, is typically viewed as a stabilizing oxide that maintains the dispersion of Cu and Zn. However, considering the high reactivity of alumina toward many small molecules, including CH₃OH (vide infra),^[45-48] e.g. the dehydration of CH₃OH to dimethyl ether (DME),^[46] one may wonder about the involvement of alumina during the hydrogenation of CO₂. In fact, studies on CO₂ hydrogenation catalysts based on alumina-supported Cu nanoparticles are rare, and the influence of CH₃OH or the effect of the Lewis acidic support on activity/product selectivity are often overlooked.^[15, 49-55]

In order to understand the role of alumina, we reasoned that studying alumina-supported Cu nanoparticles in the absence of zinc oxide would be ideal. We thus prepared small and narrowly dispersed Cu nanoparticles on Al₂O₃ via SOMC.^[56-57] Using detailed catalytic studies augmented by ex-situ solid-state NMR, operando transient diffuse reflectance infrared spectroscopy (DRIFTS) and DFT modelling, we demonstrate that Cu/Al₂O₃ is a highly effective CO₂ hydrogenation catalyst in forming CH₃OH that is further converted into dimethyl ether (DME). We also show however that Cu/Al₂O₃ catalyzes the conversion of CO₂ to CO, and the formation and decomposition of methyl formate into CO, thus providing key information about the role of alumina in determining the selectivity in CO₂ hydrogenation.

2 Results and Discussion

2.1 Catalyst Synthesis and Characterization

Copper nanoparticles supported on alumina are prepared via SOMC^[56] that involves grafting [Cu_n(Mesityl)_n] (n=2,4,5) in toluene on γ -alumina dehydroxylated at 500 °C (Al₂O₃-500, 2.1 OH nm⁻²), followed by a reduction step under H₂ at 500 °C, yielding Cu_{Xwt}/Al₂O₃ where X specifies the Cu weight loading (Figure 1a). The copper loading is controlled by grafting a specific amount of [Cu_n(Mesityl)_n] (n=2,4,5) per nm² yielding catalysts with 2.4 and 3.8 wt% copper, referred to as Cu_{2.4wt}/Al₂O₃ and Cu_{3.8wt}/Al₂O₃, respectively (Table 1). After the grafting step, the IR spectrum shows the consumption of the surface Al-OH groups (bands above 3500 cm⁻¹) and the appearance of C-H stretching bands at around 3000 cm⁻¹ (Figure 1b and Figure A.1 for Cu_{3.8wt}/Al₂O₃). Subsequent treatment under H₂ at 500 °C restores the Al-OH groups

while all C-H stretching bands disappear (Figure 1b), consistent with the removal of all organic ligands.

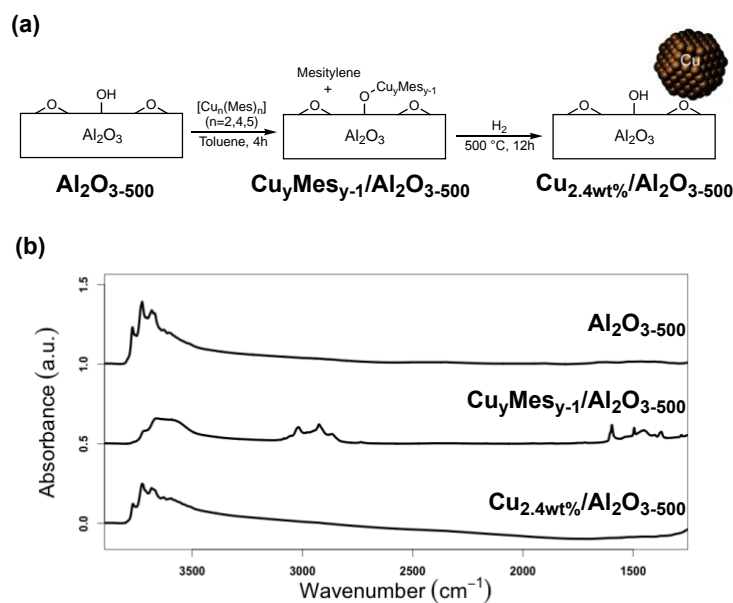


Figure 1. (a) Reaction scheme for the synthesis of copper nanoparticles on $\text{Al}_2\text{O}_3\text{-500}$ with a Cu loading of 2.4 wt% with Mes representing the mesitylene ligand. (b) IR spectra of grafting and reduction of $[\text{Cu}_n(\text{Mesityl})_n]$ ($n=2,4,5$) on $\text{Al}_2\text{O}_3\text{-500}$.

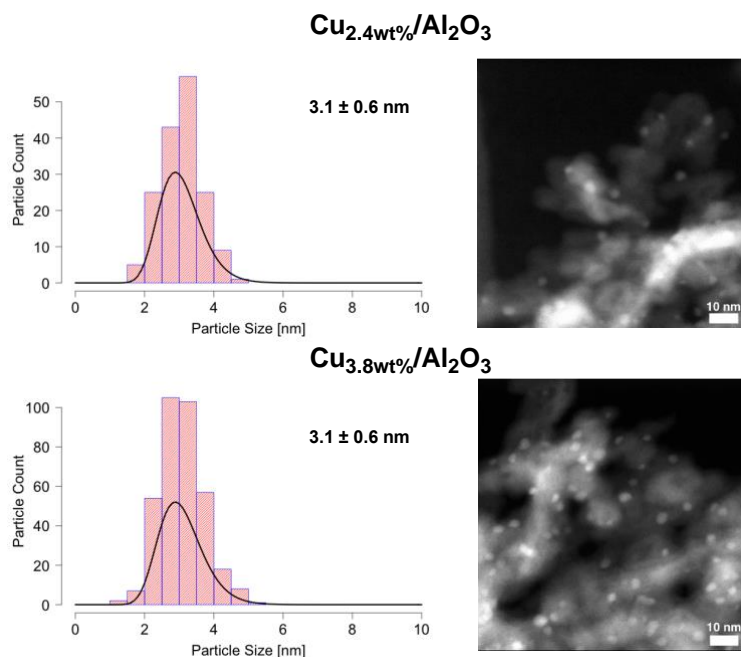


Figure 2. HAADF-STEM and particle size distribution (particle counts > 150) of $\text{Cu}_{x\text{wt\%}}/\text{Al}_2\text{O}_3$ catalysts.

Dark-field scanning transmission electron microscopy indicates the formation of copper nanoparticles in both samples with sizes of 3.1 ± 0.6 nm for Cu_{2.4wt%}/Al₂O₃ and Cu_{3.8wt%}/Al₂O₃, respectively (Figure 2). The dispersal of copper particles takes place without the change in specific surface area that is ca. 140 m² g⁻¹ according to N₂ adsorption/desorption isotherms (77 K) for both samples. In addition, powder X-ray diffraction shows only the crystalline phase of γ -Al₂O₃ and the absence of crystalline copper, consistent with the presence of small nanoparticles (Figure A.2). N₂O chemisorption shows that the copper surface site concentration is 40 $\mu\text{mol g}_{\text{cat}}^{-1}$ and 67 $\mu\text{mol g}_{\text{cat}}^{-1}$ for Cu_{2.4wt%}/Al₂O₃ and Cu_{3.8wt%}/Al₂O₃, respectively (Table 1), consistent with a similar particle size distribution by microscopy and dispersion by H₂ chemisorption (62 $\mu\text{mol g}_{\text{cat}}^{-1}$ and 86 $\mu\text{mol g}_{\text{cat}}^{-1}$ H₂ uptake for Cu_{2.4wt%}/Al₂O₃ and Cu_{3.8wt%}/Al₂O₃, respectively – Figure A.3), where a higher H₂ uptake is observed compared to N₂O. Overall using the methodology of grafting an organometallic precursor followed by reduction under H₂ leads to the formation of copper nanoparticles with similar dispersions, for both copper loadings.

Table 1. Physicochemical properties of copper-based catalysts.

Entry	Support	Cu content ^[a] [wt%]	Specific surface area ^[b] [m ² g ⁻¹]	Cu surface area based on N ₂ O ^[c] [$\mu\text{mol g}_{\text{cat}}^{-1}$]	Cu surface area based on H ₂ ^[d] [$\mu\text{mol g}_{\text{cat}}^{-1}$]	Particle size distribution ^[e] [nm]
1	Cu/SiO ₂ ^[f]	4.19	197	50/34	NA	2.9 ± 1.3
2	Cu _{2.4wt%} /Al ₂ O ₃	2.40	141	45/40	62	3.1 ± 0.6
3	Cu _{3.8wt%} /Al ₂ O ₃	3.81	139	66/67	86	3.1 ± 0.6

[a] Determined by ICP-OES; [b] Determined from N₂ physisorption applying the BET theory; [c] Measured on fresh/spent catalyst, assuming a 1:2 stoichiometry between N₂O and Cu surface sites; [d] Measured on fresh catalyst, assuming a 1:2 stoichiometry between H₂ and Cu surface sites [e] Determined by TEM on the fresh catalyst. [f] Reference [13].

2.2 Catalytic Studies

The thus-prepared catalysts were then evaluated in CO₂ hydrogenation in a fixed-bed flow reactor at 230 °C and 25 bar producing CH₃OH, CO and DME as the main products (Figure 2). Since DME is likely formed from the secondary reaction of CH₃OH on Al₂O₃ (vide infra),^[46] we compare catalysts based on the combined formation rate of CH₃OH and DME (1:2

DME:CH₃OH stoichiometry), expressed in g CH₃OH g_{Cu-1} h⁻¹. The catalysts are compared to the Cu/SiO₂ benchmark catalysts prepared via SOMC that also contain similar particles sizes according to TEM (Table 1).^[13] The formation rates are given by extrapolation to 0 s g_{cat} ml⁻¹ contact time (Figure A.4-A.8) from catalytic results reaching up to 7% conversion (Figure A.9). The equilibrium conversion under the given reaction conditions is around 17% including the dehydration of CH₃OH to DME and 15% without. For Cu_{2.4wt%}/Al₂O₃ the intrinsic CH₃OH formation rate is around three times greater (0.89 g g_{Cu-1} h⁻¹) than with Cu/SiO₂ (0.27 g g_{Cu-1} h⁻¹), a non-Lewis acidic support. This increase in CH₃OH formation rate is paralleled by an increased intrinsic CO formation rate, of ca. four times (1.04 g g_{Cu-1} h⁻¹) for Cu_{2.4wt%}/Al₂O₃ compared to Cu/SiO₂. Increasing the Cu loading to 3.8 % (Cu_{3.8wt%}/Al₂O₃) has hardly any effect on the intrinsic CH₃OH formation rate, while the CO formation rate decreases (0.73 g g_{Cu-1} h⁻¹) (Figure 2). Overall, Cu/Al₂O₃ catalysts show higher formation rates for both CH₃OH and CO compared to Cu/SiO₂ while generating large amounts of DME that is not observed for Cu/SiO₂ as a result from the subsequent dehydration of CH₃OH on alumina.^[46] While DME appears as a primary product as indicated by an intrinsic formation rate greater than zero; this is most likely due to strong adsorption of CH₃OH allowing the further dehydration to DME prior to desorption (*vide infra*). As proposed for Cu/ZrO₂ and related systems,^[12-13] Lewis acidic supports likely promote the formation of CH₃OH, but stronger Lewis acids such as those found on Al₂O₃ are also able to further catalyze the dehydration of CH₃OH to DME.^[46] Interestingly, Cu/Al₂O₃ also promotes CO formation, which is not observed for Cu/ZrO₂.^[12] The CO and CH₃OH (including DME) formation rate decreases at higher conversions, i.e., longer contact time, consistent with the involvement of Lewis acidic sites and their inhibition by the coordination of reaction intermediates/products (Figure A.10-A.14). To further investigate the role (promotional effect) of Al₂O₃ on the observed selectivity patterns, in particular with respect to the increase of CO selectivity, not observed for Cu/ZrO₂, CO₂ hydrogenation was also investigated with physical mixtures of Cu/SiO₂ with varying amounts of Al₂O₃, while keeping the amount of copper constant. We note that Al₂O₃ in the absence of Cu does not show any catalytic activity in CO₂ hydrogenation at 230 °C. The CO₂ hydrogenation carried out with a physical mixture consisting of a 5:1 (w/w) ratio of Cu/SiO₂:Al₂O₃ shows a similar formation rate for hydrogenated products (CH₃OH) as observed for Cu/SiO₂ but includes the formation of DME. In addition, the formation rate of CO is ca. doubled (0.49 g g_{Cu-1} h⁻¹) by comparison with Cu/SiO₂, leading to an overall CO selectivity increase. Increasing the ratio of Al₂O₃ with Cu/SiO₂ to 1:1 (w/w) further increases the CO formation rate marginally (0.53 g g_{Cu-1} h⁻¹), implying that a larger amount of Al₂O₃ does not further affect the rate determining step for CO

formation. The overall CH₃OH formation rate remains similar as found for Cu/SiO₂ with a rate of ca. 0.25 g g_{Cu}⁻¹ h⁻¹ and a higher ratio for DME vs. CH₃OH (Figure 2). The same trends are observed when formation rates at higher conversions (1% and 2%) are considered, with the only observation being the decrease in formation rates for all the products due to product inhibition (Figure A.15). All the data are also recorded at conversions that are far away from equilibrium, with the catalytic reaction being kinetically controlled. Thus, Al₂O₃ is responsible for the increased formation rate of CO in the physical mixtures between Cu/SiO₂ and Al₂O₃, while it promotes both CO and CH₃OH formation rates in Cu/Al₂O₃ pointing out the role of interfacial sites in this reaction. In fact, for Cu_{Xwt}/Al₂O₃ (X = 2.4 and 3.8) samples (Figure 2), the CH₃OH formation rates are similar when normalized by the amount of copper due to having similar copper dispersions for both samples and the formation rate of CO decreases with higher copper loading but is proportional to the mass of the catalyst (Figure S16).

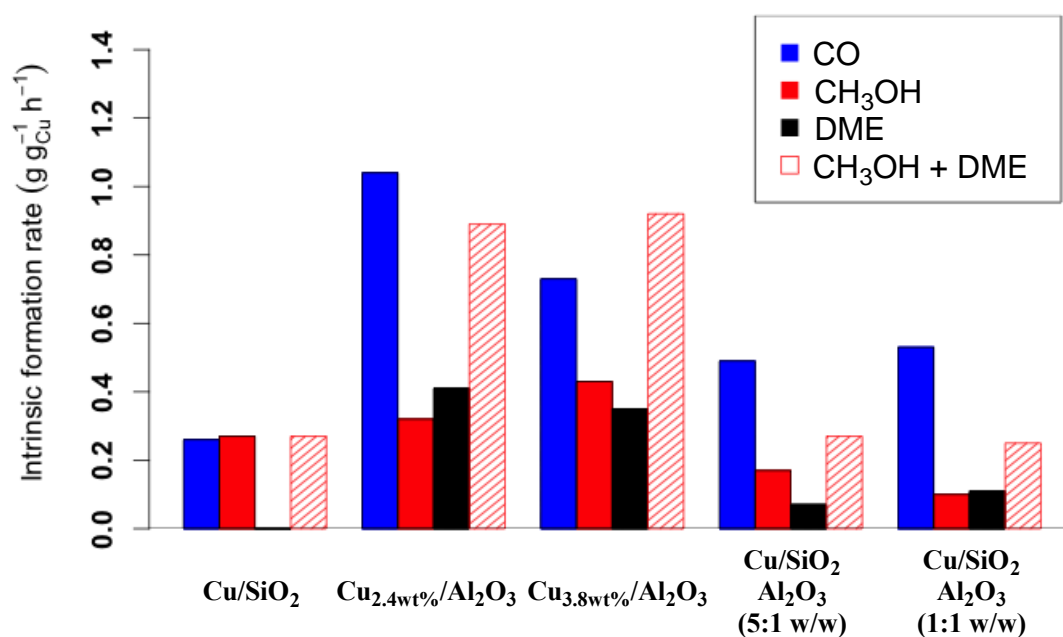


Figure 2. Intrinsic formation rates for Cu/SiO₂ and Cu/Al₂O₃ as well as physical mixtures of Cu/SiO₂ and Al₂O₃ for the formation of CO (blue), CH₃OH (red), DME (black) and overall CH₃OH formation (CH₃OH + DME red-dashed).

Since Al₂O₃ itself is not active for the RWGS reaction, these data also suggest that Al₂O₃ is able to mediate the formation of CO from products resulting from the hydrogenation of CO₂ on Cu/SiO₂. Plotting the ratio of CH₃OH with DME formation rates shows a clear correlation between the products, expected from DME originating from the dehydration of CH₃OH (Figure A.17). The ratio between CH₃OH and CO formation rates normalized by both the copper

loading and mass of catalyst does not show a clear correlation amongst different catalysts (Figure A.18-A.19), thus hinting to multiple reaction pathways for CO formation.

2.3 Mechanism for the Formation of Products and Byproducts – DME and CO – on Al₂O₃

In order to identify possible reaction intermediates formed on Cu_{2.4wt%}/Al₂O₃, we used solid state NMR (Magic Angle Spinning (MAS) ¹H- and ¹³C-ssNMR as well as ¹H-¹³C HETCOR ssNMR after reaction with 5 bar of ¹³CO₂:¹H₂ (1:3 ratio) at 230 °C for 12 hours in a batch reactor (for details see Chapter A6), followed by evacuation of the gas phase at room temperature under high vacuum (10⁻⁵ mbar). The ¹H-¹³C HETCOR spectrum shows the presence of two correlation peaks at 8/170 ppm and 2.9/48 ppm (Figure 3a), consistent with the formation of formate and methoxy species on the oxide support as previously observed on Cu/ZrO₂.^[12-13] No adsorbed DME (expected at around 60 ppm in ¹³C-ssNMR) is observed (Figure A.20), while both DME and CH₃OH are observed in the gas phase by ¹³C solution NMR following the condensation of the gas phase after reaction in deuterated benzene (C₆D₆) (Figure 3b). The formation and desorption of DME is in fact also evidenced by transmission IR, where upon adsorption of 60 mbar of CH₃OH on Al₂O₃ and heating to 200 °C; the presence of H₂O and CH₃OH can be observed, but not adsorbed DME as evidenced by the absence of signals at around 1160 cm⁻¹ (Figure A.21) which is only observed in the gas phase by NMR upon condensation of the gas phase in C₆D₆ (Figure A.22), showing that DME is more weakly adsorbed on the catalyst surface than other reaction intermediates and products such as CH₃OH or H₂O.^[46] This is consistent with the strong adsorption of CH₃OH and the appearance of DME as a primary product generated by subsequent dehydration of CH₃OH.

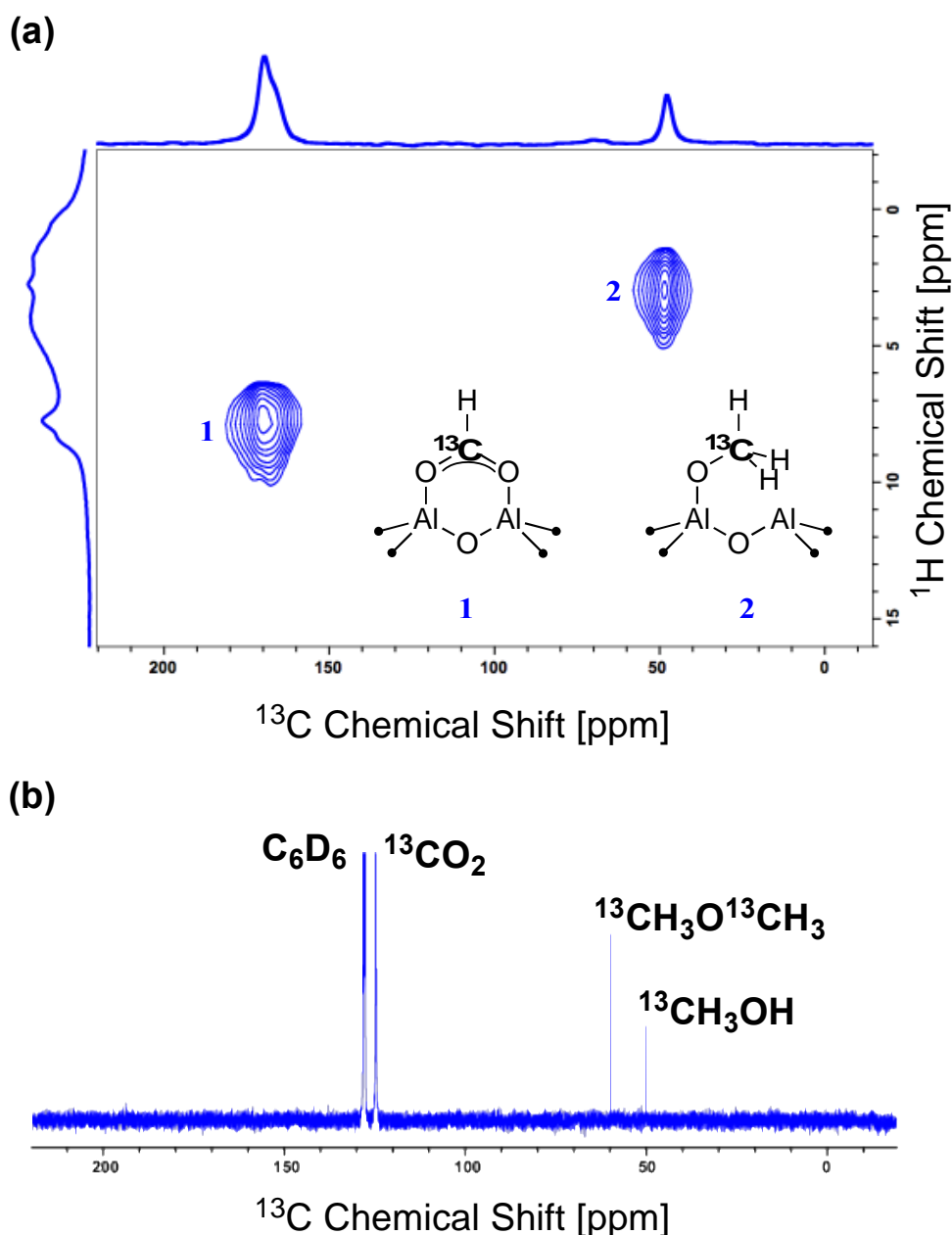
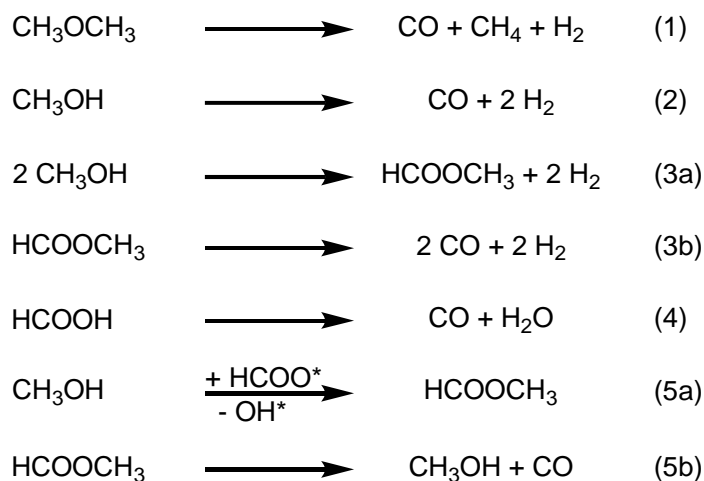


Figure 3. (a) Ex-situ MAS-NMR ^1H - ^{13}C HETCOR spectra of $\text{Cu}_{2.4\text{wt}\%}/\text{Al}_2\text{O}_3$ reacted with $\text{CO}_2:\text{H}_2$ (1:3) at 5 bars for 12 hours and 230 °C. (b) Solution ^{13}C NMR of the gas phase of $\text{Cu}_{2.4\text{wt}\%}/\text{Al}_2\text{O}_3$ after reaction recorded in C_6D_6 .

CO can originate from several reaction pathways mediated by Al_2O_3 . Among possible explanations, Al_2O_3 contains highly reactive surface sites able to activate small molecules that can mediate the formation of CO through the decomposition of DME/ CH_3OH or the formation and the subsequent decomposition of formic acid/methyl formate (Scheme 1).^[47, 58] The decomposition of DME into CO requires concomitant formation of CH_4 (eq. 1),^[47] a product that is only observed in trace amounts under the investigated reaction conditions. Alternatively, the direct decomposition of CH_3OH to CO (eq. 2) or the formation of methyl formate from two

equivalents of CH₃OH followed by decomposition to CO (eq. 3) are not likely either, due to a higher CO₂ conversion for the Cu/SiO₂ and Al₂O₃ physical mixtures. Similarly, the proposed decomposition of CH₃OH and methyl formate according to eq. 2 and 3 would lead to the formation of H₂, which is thermodynamically less likely considering the low conversion and since the use of high pressure of H₂ (15 bar) disfavor a reaction that generates H₂. CO could also arise from the decomposition of formic acid that can potentially be formed on Cu/SiO₂ and subsequently decomposes on Al₂O₃ to CO and H₂O (eq. 4).^[21] It is for example known that formic acid can decompose to CO and H₂O on Al₂O₃ or SiO₂.^[21] Finally, methyl formate formed upon reaction of CH₃OH with surface formate species (denoted as HCOO*) generating a surface hydroxyl group (OH*), could subsequently decompose to form CH₃OH and CO (eq. 5). In fact, surface formate species are observed by solid-state NMR upon reaction of the Cu/Al₂O₃ or Al₂O₃ with 5 bar of ¹³CO₂:H₂ (1:3) at 230 °C for 12 hours (Figure 3a and Figure A.23-A.24). The formation of methyl formate is known to occur during CO₂ hydrogenation at high pressures (300 bar) and can be further promoted by cofeeding CH₃OH,^[59] but its decomposition is likely hindered at high pressures (300 bars).^[49]

Scheme 1. Possible reaction pathways for the formation of CO.



Reaction of methyl formate with Al₂O₃ at 230 °C also yields CH₃OH, DME and CO, consistent with the decomposition of methyl formate into CH₃OH and CO at 230 °C with the concomitant dehydration of CH₃OH into DME under reaction conditions (Figure A.25). Furthermore, methyl formate is also shown to decompose to CO and CH₃OH on Cu/Al₂O₃ (Figure A.26).

In order to understand additional reaction pathways besides the decomposition of formic acid forming CO and H₂O on Al₂O₃ based catalyst,^[15-16, 21] the effect of CH₃OH and its interaction with surface species for the formation of CO is further investigated. Thus, Cu_{3.8wt%}/Al₂O₃ was studied by transient operando diffuse reflectance infrared spectroscopy (DRIFTS) with online activity monitoring to identify correlation between the gas phase composition with the concentrations of adsorbed intermediates. The changes in the IR spectrum and the gas phase composition are monitored at 230 °C and 5 bar under a transient condition, i.e. switching the atmosphere between a mixture of CO₂ and H₂ and a mixture of CO₂, H₂ and CH₃OH (vapor) (Figure 4a). In the latter atmosphere, concentrations of CH₃OH, DME, CO and methyl formate increased (Figure 4b and A.27), confirming that the formation of DME, CO and methyl formate are largely influenced by the concentration of CH₃OH. The IR spectrum in the region of 1000-1900 cm⁻¹ shows two formate species that are behaving kinetically different (at ca. 1640 and 1670 cm⁻¹) based on multivariate curve resolution analysis.^[60] The two formate species are proposed to be Al₂O₃ bound formates^[16] and are quickly decreasing in intensity when CH₃OH is present (Figure 4c and A.28), in line with the rapid formation of methyl formate. In addition, when switching between CO₂/H₂ and Ar, the concentration of the formate species at ca. 1640 cm⁻¹ is decreasing with a slower rate (Figure 4d blue), indicating that CH₃OH can indeed facilitate the removal/reaction of this surface formate species. This is further supported by a similar profile of the IR signals observed between 2500 and 3100 cm⁻¹ corresponding to methoxy species (Figure A.29-A.30). In addition the evolution of methoxy species are shown in the region between 2500 and 3100 cm⁻¹: with a decrease in concentration of methoxy surface species when switching between CO₂/H₂/CH₃OH and CO₂/H₂ (Figure A.29) vs. an increase in concentration of methoxy surface species when switching between Ar and CO₂/H₂ (Figure A.30). Overall, it shows the possible formation of methyl formate from CH₃OH that could then further decompose to CO on Cu_{3.8wt%}/Al₂O₃.

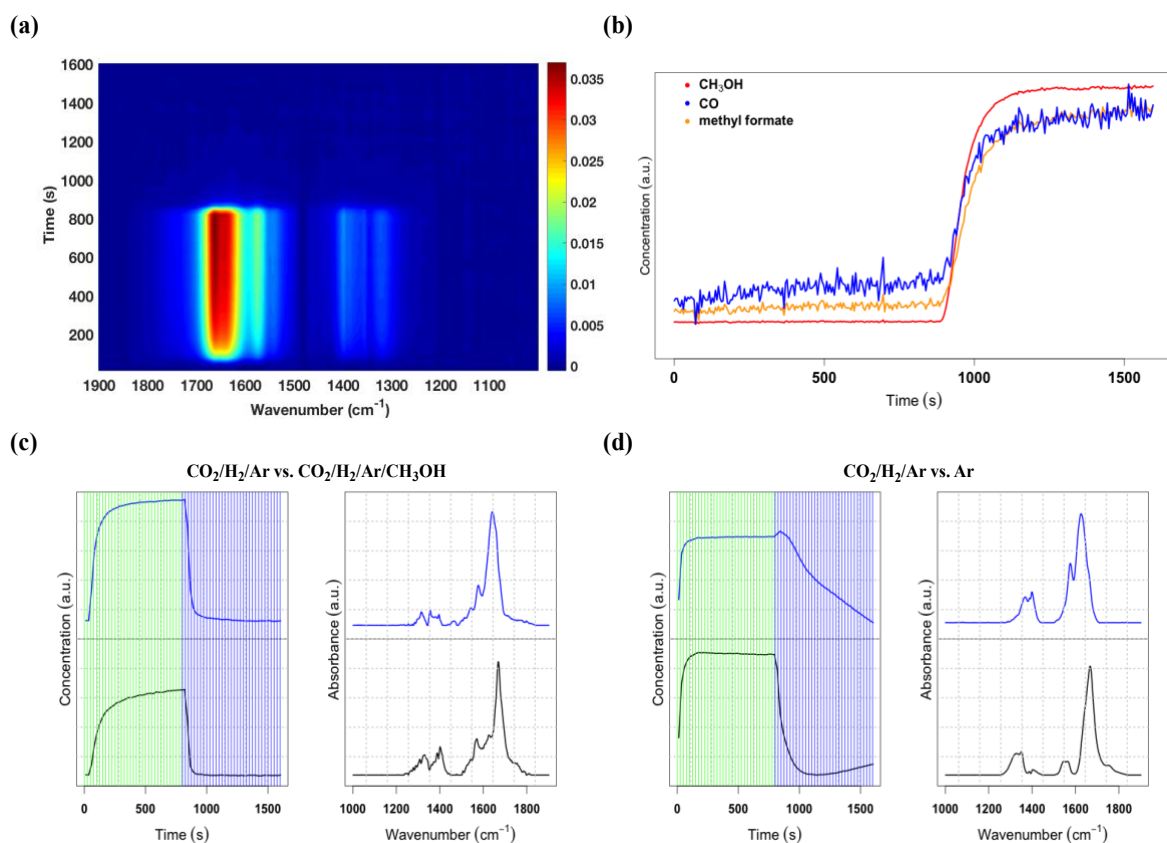


Figure 4. (a) Evolution of surface species between 1000 and 1900 cm⁻¹ during transient operando DRIFTS experiments at 5 bar and 230 °C switching between CO₂/H₂/Ar and CO₂/H₂/Ar/CH₃OH for Cu_{3.8%}/Al₂O₃. (b) Gas phase concentration of CH₃OH, methyl formate and CO between gas mixtures of CO₂/H₂/Ar and CO₂/H₂/Ar/CH₃OH. (c) (left) Concentration profile of two surface species (wavenumber 1000-1900 cm⁻¹) corresponding to (right) component spectra in blue and black obtained by MCR analysis when switching between gas mixtures of CO₂/H₂/Ar (green) and CO₂/H₂/Ar/CH₃OH (blue). (d) (left) Concentration profile of two surface species (wavenumber 1000-1900 cm⁻¹) corresponding to (right) component spectra in blue and black obtained by multivariate spectra analysis when switching between gas mixtures of CO₂/H₂/Ar (green) and Ar (blue).

2.5 Role of the Metal/Oxide Interface on CH₃OH and CO Formation

In order to obtain further information about the reaction mechanism, possible active site structures, and the role of perimeter sites around the copper nanoparticle, we investigated potential reaction pathways via a computational approach. The Cu/Al₂O₃ catalyst is modeled by placing a Cu₆₇ particle (corresponding to ca. 1 nm diameter) on the most abundant (110)-facet of γ -Al₂O₃ (Figure 5a). This facet exposes different aluminum sites with different coordination number that can be found at the periphery (interface) between Cu and Al₂O₃. Due

to the copper nanoparticle size, the interface between the metal and the support can have various interfacial sites that are further investigated by DFT calculations. They are denoted **Al(III)**, **Al(IVA)** and **Al(IVB)**, the number indicating the coordination number and the letter describing two types of four-coordinated sites (Figure 5a).^[45, 61] First, CO₂ can adsorb on these interfacial sites to generate bent monodentate (Figure 5b – **Al(III)**) or bridging (μ_2) CO₂ species by involving two neighboring aluminum sites (Figure 5b - **Al(III)-Al(IVB)** and **Al(IVA)-Al(IVA)**) with CO₂ adsorption free energy (calculated at 500 K) ranging from $\Delta_rG = -59$ to 63 kJ mol⁻¹ (Figure 5b and Table A.1), while CO₂ does not interact with the Cu(111) surface and remains linear ($\Delta_rG = +46$ kJ mol⁻¹). This adsorbed CO₂ at the interface between copper and Al₂O₃ can then further react with surface Cu-hydrides generated by splitting H₂ on the copper particle forming CH₃OH or CO (Figure 5c, Figure A.31-A.32 and Table A.2), similar to the pathway proposed by DFT calculation for Cu/ZrO₂.^[12] CO₂ is hydrogenated to formate (HCOO*), acetal (CH₂OO*) and (CH₂OOH*) upon which the C-O bond is broken forming CH₂O* and OH*. Further hydrogenation yields methoxy (CH₃O*) and hydroxide (OH*) (Figure 5c) and finally CH₃OH and H₂O that can desorb from the catalyst, closing the catalytic cycle. Alternatively, the CO₂ adsorbed at the interface of the copper nanoparticle and Al₂O₃ can directly split into CO* and O* (Figure 5b). The O* is located at the interface between copper and Al₂O₃ while CO coordinated on copper that desorbs. Further hydrogenation yields H₂O that desorbs from the catalyst, similar to what was shown on Ni/Al₂O₃, where the interfacial sites are playing a key role during the RWGS reaction.^[62-63]

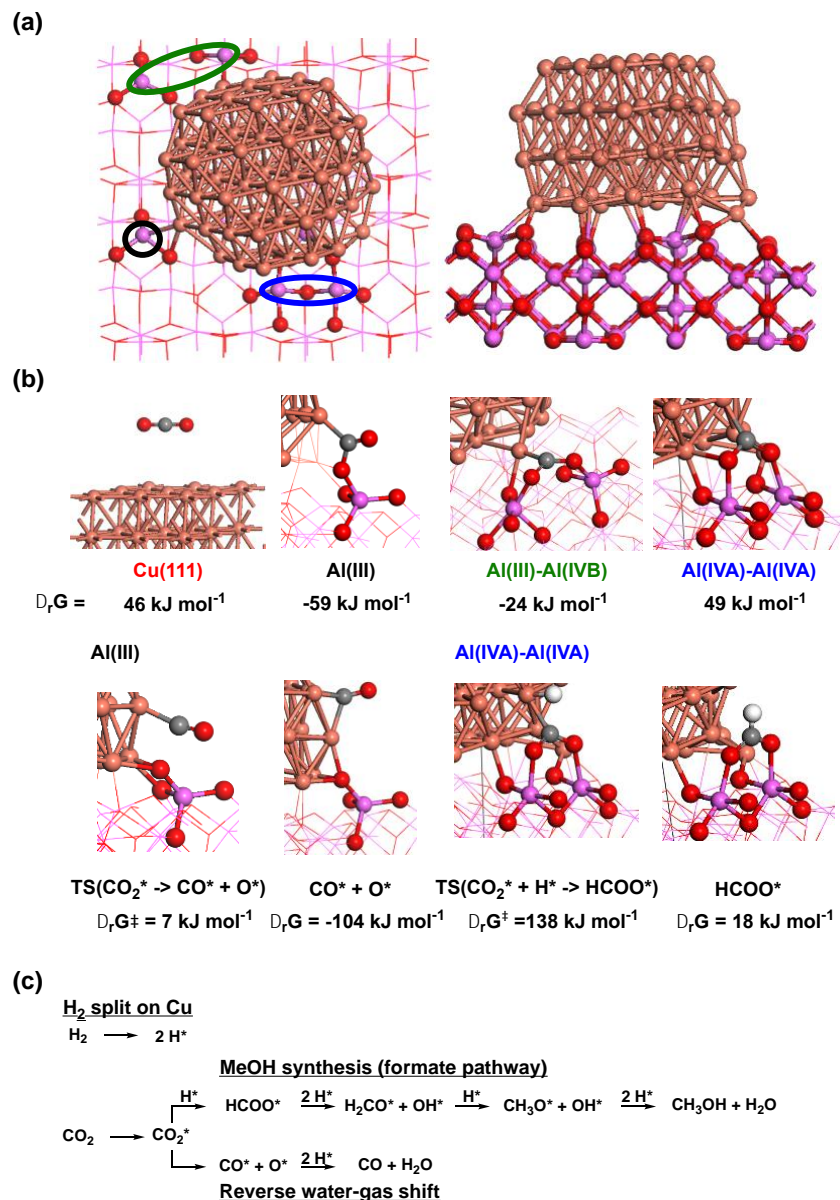


Figure 5. (a) Top (left) and side (right) view of the computational model consisting of the (110) facet of γ - Al_2O_3 and a Cu_{67} particle with the aluminum interfacial sites circled for **Al(III)** (black), **Al(III)-Al(IVB)** (green) and **Al(IVA)-Al(IV)** (blue). (b) Structure and adsorption free energy ($\Delta_r G$) calculated at 500 K in kJ mol^{-1} of CO_2 interacting with the **Cu(111)** facet and the interfacial sites with respect to gas phase CO_2 . **Al(III)** site (black circle), an **Al(III)** site in close proximity to an **Al(IVB)** site (green circle), and two **Al(IVA)** sites in close proximity (blue circle). Transition state for the formation of $\text{CO}^* + \text{O}^*$ and HCOO^* on **Al(III)** and **Al(IV)-Al(IV)**, respectively. (c) Reaction mechanism for the formation of Cu-H, CH_3OH via the formate pathway, and CO.

Overall, sites where CO₂ is coordinated in a monodentate geometry as on **Al(III)** appears to favor CO formation, whereas CO₂ adopting a bridging (μ_2) coordination favors the formation of HCOO* and ultimately CH₃OH on **Al(IV A)-Al(IV A)**. Thus, depending on the nature of the aluminum site it can either favor CH₃OH or CO. This can be explained by the geometry of CO₂ (Figure 5b). Bonding in a monodentate geometry allows to easily break the C-O bond leading to the RWGS reaction being favored, while having a bridging (μ_2) coordination CO₂* consist of a geometry that resembles this of formate species (HCOO*), hence the low activation barrier for its formation. It shows that CO₂ hydrogenation at the Cu/Al₂O₃ interface lowers the activation energy for both CH₃OH and CO in comparison to the **Cu(111)** surface (for further details see Chapter A6). This is consistent with the increase in CH₃OH and CO formation rate found experimentally and in line with the inhibition for both the CH₃OH and CO formation at longer contact times due to coordination on Lewis acid sites by reaction products (H₂O/CH₃OH) that have a stronger adsorption energy than CO₂. The formation of DME is shown not to require the presence of copper and can solely take place on the Al₂O₃ surface, where by DFT calculation, DME is preferentially formed on more strongly Lewis acidic sites (Scheme A.1). In addition, the most strongly adsorbed reaction intermediates determined by DFT calculation (HCOO* and CH₃O*) are the same intermediates observed with ex situ solid state NMR experiments (vide supra).

3 Conclusion

Copper nanoparticles (2-4 nm) supported on Al₂O₃ is a bifunctional catalyst that is particularly active toward the catalytic hydrogenation of CO₂ into CH₃OH, DME and CO, in contrast to what is observed with SiO₂ or ZrO₂ supports that show low activity and selectivity or promote only CH₃OH formation rate, respectively. The formation of CH₃OH and CO as well as the further dehydration of CH₃OH to DME is due to the strongly Lewis acidic Al₂O₃ support that promotes both of these reactions. The observed promotional effect is traced back to specific interfacial sites present between copper and Al₂O₃, that favors CH₃OH formation via formate intermediates, but also the direct conversion of CO₂ to CO. In addition, these Lewis acid sites open additional reaction pathways, converting surface formate intermediates upon reaction with CH₃OH to methyl formate that can then further decompose into CO. This study thus showcases how the Al₂O₃ support can participate in the formation of a broad range of products, increasing both CH₃OH and CO production rates and also helps rationalizing the effect of Lewis acidic oxide supports on the catalytic properties of Cu nanoparticles in CO₂ hydrogenation. Such

information provides guidelines on ways to tune the catalytic performances of CO₂ hydrogenation catalysts that we are currently exploring.

4 Experimental Section

General: SiC (FisherEU) and CH₃OH (Acros Chemicals) were used as received. Pentane and toluene were purified over two solvent purification alumina columns (MBraun) and degassed prior to use. Methyl formate (Acros Chemicals) was distilled over P₂O₅ and degassed. H₂ for catalyst preparation was purified over activated R3-11 BASF catalyst and activated 4 Å molecular sieves. Al₂O₃ (TH 100/150) was provided from Sasol and calcined at 500 °C under synthetic air, followed by evacuation under high vacuum and stored in an argon filled glovebox (denoted as Al₂O₃₋₅₀₀). Unless otherwise specified all preparations of catalysts were carried out under argon using standard Schlenk techniques and gloveboxes. [Cu_n(Mesitylene)_n]_[64] and Cu/SiO₂_[13] were synthesized according to literature procedures and stored in an argon filled glovebox. All the details concerning material characterization and catalytic testing are described in chapter 2,3 and 4.

Representative procedure for supported copper nanoparticle synthesis: A solution of [Cu_n(Mesitylene)_n] (220 mg, 0.24 mmol (for n = 5)) in 20 mL of toluene was added to 2 g of the Al₂O₃ dehydroxylated at 500 °C wetted with toluene. The suspension was stirred for 4 hours, washed three times with toluene (5 mL) and dried at 10⁻⁵ mbar for 1 hour. The solid was then reduced under H₂ at 500 °C for 5 hours (100 °C h⁻¹) cooled down to room temperature under H₂, evacuated under high vacuum (10⁻⁵ mbar) and stored in an argon filled glovebox. Grafting on a NMR scale using ferrocene as internal standard, shows the release of 0.4 equiv. mesitylene and maximal consumption of 0.24 equiv. [Cu_n(Mesitylene)_n] (for n = 5) with respect to the OH density (0.52 mmol/g), in line with the maximum Cu loading of 3.8 wt%.

Procedure for methanol dehydration: A self-supporting pellet of Al₂O₃₋₅₀₀ in a reactor equipped with CaF₂ windows were contacted with 60 mbar of CH₃OH and heated to 200 °C for 30 min after which the IR spectrum of the pellet was recorded. Reference spectra of Al₂O₃₋₅₀₀ and Al₂O₃₋₅₀₀ contacted with DME (30 mbar) were recorded in the same fashion.

Representative procedure for methyl formate decomposition: To 50 mg of catalyst in a volume of 15 cm³ was introduced 60 mbar of methyl formate and heated to 230 °C using a sand bath (300 °C/h). The gas phase was analyzed by GC before heating, after 30 minutes while heating and 2 hours after the start of the experiment.

4.1 Transient DRIFTS and MCR Analysis

The samples were ground to fine powders and placed in a custom-made reaction cell with a ZnSe window that allowed to pressurize the system to 5 bar. The material was then reduced under a stream of H₂ at 300 °C for 1 hour. Transient DRIFTS studies were then performed by switching two different reactant gases (Ar, Ar/CH₃OH, CO₂/H₂/Ar (1:3 ratio CO₂:H₂ with 4% Ar) or CO₂/H₂/Ar/CH₃OH) that periodically flow through the catalyst as previously reported.^[59] For the gases containing CH₃OH, the gases were passed through a saturator containing CH₃OH at room temperature. Transient experiments were performed at 230 °C and 5 bar by periodically changing between two stream of gases every 800 s, to obtain four cycles (4 x 1600s). The products were analyzed using a mass spectrometer (OmniStar GSD 320 O series, Pfeiffer Vacuum) or by transmission IR (ALPHA IR spectrometer, Bruker) in *operando* studies. The last three cycles were averaged to enhance the signal to noise ratio. Multivariate spectral analysis was performed by means of multivariate curve resolution (MCR) as described elsewhere.^[60]

4.2 Computational Details

Periodic DFT calculations were carried out with Vienna Ab Initio Simulation Package (VASP) code^[65-67] using the projector augmented wave (PAW) method with a plane wave energy cutoff of 400 eV and the PBE exchange-correlation functional.^[68] The criterion convergence chosen for the SCF cycle was 10⁻⁵ eV, and optimizations were considered converged once the forces on all atoms were lower than 0.1 eV.Å⁻¹. To model the alumina surface, we considered a slab of the (110) termination of γ -alumina. The slab was 16.1 x 16.8 Å large, and 5 Å thick (144 atoms, 32 Al₂O₃ units), with a vacuum separation of ca 15 Å. The two lowest atomic layers were frozen during optimizations and transition state calculations. The Brillouin zone was sampled with a 3 x 3 x 1 k-point grid. Electron occupancies were determined according to a gaussian scheme with an energy smearing of 0.1 eV. For the supported copper particle, a Cu₆₇ cluster of half-truncated octahedron shape from Cu fcc structure was deposited on the surface. The Cu/Al₂O₃ model was optimized before studying the adsorption and reactivity of CO₂ and H₂. Cu(111) was simulated using a periodic 3 x 3 four-layer slab consisting of 36 Cu atoms with a vacuum separation of 15 Å. During optimization, the bottom Cu(111) layer was frozen. The Brillouin zone was sampled with a 3 x 3 x 1 k-point grid. Electron occupancies were determined according to a Methfessel-Paxton scheme with an energy smearing of 0.2 eV. In order to correct for errors in the gas-phase thermochemistry, the energy of the gas phase CO was reduced by 50 kJ/mol.^[62] Transition states were determined using the Climbing Image

Nudge Elastic Band (CI-NEB) method^[69] with 8 images and were confirmed by the presence of a single negative mode in frequency analysis. Thermodynamic calculations were performed by including enthalpic and entropic contributions to obtain the Gibbs free energies at 500 K from vibrational frequencies from gas-phase, adsorbed species and transition states reported elsewhere.^[12] The term $\Delta_r G$ corresponds to the relative free energy between the adsorbed molecule or reaction intermediate and the term $\Delta_r G^\ddagger$ corresponds to the relative free energy of the transition state with respect to the free energy of CO₂ and H₂ in the gas phase and Cu/Al₂O₃.

5 References

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